Wet-Strength Resins and Their Application

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INTRODUCTION

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The strength property of paper is contributed mainly by fiber–fiber bonds *(1)*. When paper is wetted in water, the swelling of fibers weakens these bonds and paper loses a substantial amount of its strength. *The Dictionary of Paper (2)* defines wet-strength paper as "a paper which has extraordinary resistance to rupture or disintegration when saturated with water." It has also been suggested that, if a paper sample retains more than 15% of its dry tensile when wetted, it can be considered to have wet-strength properties *(3)*.

The need for wet-strength paper during World War II initiated the development of wet-strength resins. In the 1940s to 1960s, the process and additives for making wet-strength paper have developed from the parchmentizing process to the extensive use of synthetic polymers—such as urea-formaldehyde, melamine-formaldehyde, and polyamide-epichlorohydrin—and other polymers such as polyethyleneimine and dialdehyde starch. These have been well documented in TAPPI Monograph No. 29, published in 1965 *(4)*. Since then, improvements have been made on these resins. New additives have been developed, and significant advances have been made in papermaking science. This chapter provides an overview of the wet-strength additives and also introduces resins which are described in detail in subsequent chapters. Topics which have significant impact in specialized applications are also discussed.

Urea-formaldehyde resins remained as one of the commercially important wet-strength resins throughout most of this period. However, regulatory compliance requirements on formaldehyde emission and the preference for application in a neutral pH papermaking condition have reduced the usage of formaldehyde resins further in the last few years. Since urea-formaldehyde and melamine-formaldehyde resins are the first generation of synthetic polymers which attained significant commercial status, the work on these resins has become classical examples to illustrate the mechanism for wet-strength development. It is also an interesting way to demonstrate the research and development activities by suppliers *(5)* and papermakers *(6)* in their successful efforts to develop resins and application technology to meet regulatory compliance requirements.

Polyamide-epichlorohydrin resins increased their share of usage at the expense of urea-formaldehyde type resins due to advantages in absorbency, softness, and neutral curing characteristics. Extensive research and development activities have been carried out in polyamide-epichlorohydrin chemistry to find improved processes and products over Keim's initial process *(7)*. Polyamine resins, which are reaction products of polyalkylenepolyamine-dihaloalkane-epichlorohydrin, have been introduced. These polyamine resins provide different curing characteristics, and treated papers have somewhat different repulping properties.

The chemistry and applications of these polyamide-epichlorohydrin and polyamine resins are of significant interest to the papermaking industry.

During the last few years, organochlorine products are of major environmental and regulatory concerns. Research has been carried out for the reduction of by-products of polyamide epichlorohydrin reaction, such as 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol. These efforts have led to polyamide-epichlorohydrin resins which have extremely low organochlorine contents and yet provide good wet-strength efficiency.

Cationic polyacrylamide-glyoxal polymers have gained significant commercial acceptance. The reaction of glyoxal-polyacrylamide with cellulose is readily reversible in the presence of water. Therefore, its wet strength is "temporary." Paper treated with this type of resin is readily repulpable. It is also reported that glyoxal-polyacrylamide increases the dry strength of paper when used in certain furnishes.

A variety of functional additives such as size, pigments, dyes, and dry-strength resins can be used in conjunction with wet-strength resins to achieve enhanced properties. It has also been realized that the colloidal chemistry in the wet end plays a key role in the optimization of wet-strength resin efficiency. Different investigators have used different techniques and devices to study the electrokinetics related to wet-end chemistry. This wealth of knowledge, though sometimes involving controversial interpretations, provides readers with information on the use of electrokinetic study for wet-strength applications.

The amount of load that paper boxes can hold and the stacking that they can sustain without breaking are recent strength requirements for paperboard containers. For boxes which are exposed to a wet environment, e.g., when used for vegetable and poultry packaging, "stiffness when wet" is a critical property. Different methods have been tried to provide this requirement. One of these processes which produced very strong paperboard involved an "impregnation" process.

A special "liquid" applicator is used to impregnate paper with a specific type of urea-formaldehyde in this process. The success of the process depends on the degree of penetration of resin into the paperboard, the temperature, the drying time of the treated board, the composition and nature of the urea-formaldehyde resin, and the coating mixture. Optimization of these parameters would provide paperboard which meets stiffness requirements without the brittleness and glueability problems.

While these commercially important wet-strength resins and technologies will be discussed in more detail in subsequent chapters in this book, there are several other developments in specialty wet-strength paper applications that are worthy of discussion here. Premium grades of paper are made to provide consumers with towels and tissues which have superior bulk, absorbency, and softness. This type of low-density paper uses papermaking technology such as dry creping and air laid papermaking *(8)*.

In conventional papermaking process, the fiber mat enters a dryer through the nip of one or two pressure rolls. The drying of the web under high pressure in the range of 300–500 psi provides the drying, the compaction, and the strength of the paper. These also introduce stiffness. A through-drying process *(9)* can be used to provide the drying efficiency while minimizing compaction and stiffness. Dry creping of the web at low moisture content of about 10% also contributes to the superior tactile properties of low-density paper. This process affects the choices and efficiency of wet-strength resins. It is believed that the desired degree of creping demands a delicate balance between the adhesion forces holding the web to the dryer surface and the release forces generated at the contacting edge of the doctor blade *(10)*. These parameters are more difficult to control in dry creping process.

During dry creping, the web surface undergoes a thermoplastic transformation causing a thin layer of coating on the dryer surface *(11)*. When a wet-strength resin is used, it will become part of the composition of this dryer coating layer. Its property and interaction with fibers will affect the balance between adhesive and releasing forces at the creping point, and the resulting creping also affects the performance of wet-strength resin. It is not unusual to observe that the wet-strength property of flat sheets (before creping) are different from that in the crepe sheets, when comparing different wet-strength resins.

The air laid or dry formed process to make "soft" paper has received significant interest by major paper companies, and a number of products have been commercialized *(12)*. A typical process is described in Kroyer's patent *(13)*. In this process, fiber is dropped into the inside of sieve-like devices. The fiber is sifted through the sieves and falls onto a moving wire below which is a suction box. After forming, binders are sprayed over the web which is then consolidated against a large, heated drum. From a functional viewpoint, binder performance is determined by its sprayability, binder cohesive and adhesive strength, and its distribution. The wet-strength property of the air formed mat can be enhanced by the use of a terpolymer *(14)*.

Another interesting wet-strength topic is premoistened paper products which retain high degree of wet strength when wet packaged in lotion composition and during usage. These products can be readily disposed of by flushing in conventional plumbing and toilet facilities. Various binders and application methods have been used for the manufacture of premoistened paper or nonwoven products *(15–17)*. A more recent patent *(18)* reports the use of a glyoxal-polyvinylalcohol copolymer to prepare a premoistened towelette or wiper-type paper product with superior wet tensile when stored in an acidic medium and during usage. Its wet strength decreased significantly in a neutral or alkaline pH for flushability. As an example, the binder can be applied to paper web by any conventional method such as by spraying, immersion, or printing and then drying by conventional papermaking facility. The treated paper web is wetted in an acidic medium comprising boric acid, surface active detergent, humectants, bactericides, and scenting or perfuming agents. A recent report also claims that the amount of boric acid can be substantially reduced by the use of a specific lotion composition *(19)*.

Polyelectrolytes have recently been used as promoters for wet-strength additives *(20)*. It is well known that anionic substances such as kraft lignin, humic acid, wood extracts *(21)*, inorganic salts, and anionic materials in the wet end have detrimental effects on wet-strength resin efficiency. With increasing use of secondary fiber and more closure of wet-end loops, there is an increased buildup of anionic contaminants and other materials such as deinking additive and ink residues. These contaminants cause operation problems such as foaming, wet-end breaks, deposits, poor retention, and poor wet-strength resin efficiency. For example, when a polyamide-epichlorohydrin resin is added to the wet end where there is a high concentration of anionic materials, its cationic charge sites are consumed by charge neutralization. Its azetidinium groups, which provide both cationic charge and crosslinking, can no longer provide effective crosslinking. This results in a loss of its wet-strength efficiency. The use of highly cationic low molecular weight polymers can overcome this problem caused by "anionic trash" and enhance the wet-strength resin efficiency *(22)*.

In this book we have summarized technology progress made in wet-strength additives and their applications in the paper industry. With the demand for increase in the use of recycled materials and the effort by the papermaking and its allied industries to use technology to manufacture environmentally friendly products and to modify working conditions to meet environmental requirements, we can expect more technological advancement in the coming years.